

# Influence of laundry effluent stability on fibre fragments identification

## Utjecaj stabilnosti efluenta od pranja tekstila na identifikaciju fragmenta vlakna

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### Abstract

Among various sources of microplastics, synthetic textiles are one of the main sources of fibrillar microplastics in aquatic environments. Fiber fragments (FFs) are mostly released during the washing process of textiles. The challenges associated with FFs characterization and quantification are related to the wide range of concentrations and degree of degradation. The laundry effluent samples present a particular challenge as they contain a residual component of the detergents used in washing processes, such as surfactants. In addition, surfactants promote the formation of aggregates composed of fibre fragments and inorganic components of the detergent (e.g. zeolites). These aggregates exhibit altered physico-chemical properties that lead to an underestimation of the fiber fragments number, which is a direct consequence of the entanglement of several fibre fragments. The aim of this study was to investigate the possibility of identifying polyethylene terephthalate fibre fragments both in water and detergent suspensions. In order to investigate the influence of solution or suspension stability on the FFs identification, the formation of aggregates was carried out with both freshly prepared but also with 5 days aged suspensions. The amount of fibre fragments in the suspensions was determined gravimetrically after membrane filtration followed by characterisation of the filter cake using an optical microscope. It was confirmed that the presence of detergents leads to aggregate formation. Furthermore, aging of the solution results in an even greater extent of aggregate formation.

**Keywords:** wastewaters; washing process; microplastics; fibre fragments; PET; detergents

### Sažetak

Sintetičke tekstilije, Među različitim izvorima mikroplastike, predstavljaju jedan su od glavnih izvora fibrilarne mikroplastike u vodenom okolišu. Fragmenti vlakana (FF) najviše se oslobađaju tijekom procesa pranja tekstila. Izazovi u karakterizaciji i kvantifikaciji FF-a povezani su s njihovim širokim rasponom koncentracija i stupnjem razgradnje. Uzorci otpadnih voda iz pranja posebno su izazvni za analizu jer sadrže ostatke deterdženata korištenih u procesu pranja, poput površinski aktivnih tvari (surfaktanata). Osim toga, surfaktanti potiču stvaranje agregata koji se sastoje od fragmenata vlakana i anorganskih komponenti deterdženta (npr. zeolita). Ujedno formirani agregati sastavljani od više zapetljanih fragmenata vlakna pokazuju promijenjena fizikalno-kemijska svojstva, što dovodi do podcjenjivanja broja fragmenata vlakana.

Cilj ovog istraživanja bio je ispitati mogućnost identifikacije fragmenata vlakana poli(etilen-tereftalata) (PET) u uzorcima vode i suspenzija deterdženta. Kako bi se istražio utjecaj stabilnosti otopine ili suspenzije na identifikaciju fragmenata vlakna, formiranje agregata provedeno je u svježe pripremljenim suspenzijama, ali i u suspenzijama koje su ostavljene da odstoje pet dana. Količina fragmenata vlakana u suspenzijama određena je gravimetrijskom metodom nakon filtracije pomoću membranskog filtra, a talog na filtru analiziran je optičkim mikroskopom. Potvrđeno je da prisutnost deterdženata dovodi do stvaranja agregata, dok starenje otopine rezultira još izraženijim stvaranjem agregata.

**Ključne riječi:** otpadne vode; proces pranja; mikroplastika; fragmenti vlakna; PET; deterdžent

## 1. Introduction

The term microplastics (MPs) refers to solid, water-insoluble plastic particles with a size between 1 µm and 1000 µm [1]. Among many other types of microplastic particles, fiber fragments are considered one of the most common forms with a total share of 35% [2]. Fiber fragments (FF), or fibrillar microplastic (FMP), are thin, elongated microplastic particles with length of 300 nm up to 15 mm whose length and diameter ratio is minimum 100 [3]. Fiber fragments are most detached as a result of mechanical abrasion of the synthetic textile materials. This usually happens during the washing process of textiles, as they're inevitably exposed to chemical, physical and mechanical stress. The tendency of these particles to migrate and microfibrillate depends on a comprehensive description of the textile including all stages of production, from the fiber to the final product. This includes the

characteristics of the textile materials: chemical structure, type and texture of the material, type of yarn and fibers contained [4, 5], material manufacturing processes and Sinner's circle factors in the washing process [6]. The released fiber fragments enter municipal water via the drain pipes of washing machines [7].

Microplastic particles pose serious environmental threat. Not only they're non-degradable, but during fragmentation leach toxic additives [8] and can also serve as a vector for the transfer of heavy metals, toxins and pathogens, endangering the health of aquatic ecosystems and indirectly that of the people who depend on these resources [9]. Therefore, MPs as emerging anthropogenic pollutants represent a serious environmental problem that requires the urgent development of technologies to remove MPs from the surrounding waters. Indeed, wastewater treatment plants (WWTPs) are the main point of entry for MPs from urban areas and industrial facilities. Recent studies have shown that an average plant

emits up to 500 million fibres per day [10].

Numerous studies have been conducted investigating the removal efficiency of WWTP technologies [11, 12]. Although existing systems may be successful in removing MPs, there is a lack of standardized methods for characterisation and quantification of microplastic fibre fragments in textile wastewaters, especially washing effluents. It is important to emphasize that this type of sample is extremely difficult to analyse. Microplastic particles, including fibre fragments, as are present in a wide range of concentrations, which also have very different shapes, sizes, densities, colors and degrees of degradation. In addition, washing effluent samples matrixes are the one's of very complex chemical composition. They very often contain released additives [8], but also remained detergent components during washing process, which interfere with further analysis. FFs have hydrophobic nature, while the addition of surfactants may change their physical and chemical properties. This result in the adsorption characteristics of inorganic substances present in detergent such as zeolites, sodium carbonate, silicates, sulphates, etc. [13]. These aggregates exhibit altered physic-chemical properties that lead to an underestimation of the FF number, which is a direct consequence of the entanglement of several fibre fragments.

Therefore, in this study we present the assessment of possibility for identification of polyethylene terephthalate (PET) fibre fragments in a presence of solid detergent. The results were compared with FMPs water suspension. We have also investigated the influence of suspension stability on the FFs identification, since the formation of aggregates may hinder PET fragments identification.

## 2. Experimental

### 2.1. Materials and chemicals

The standard polyester material (PET) used for preparation of standard solutions of following characteristics: 100% polyester fabric AISE-31 (EMPA), colour: navy, weave: canvas and area density: 189 g m<sup>-2</sup> (Figure 1).



**Figure 1.** Standard polyethylene terephthalate (PET) material used for preparation of FMP samples

For detergent suspensions preparation ECE A non-phosphate reference detergent without optical brighteners was used supplied by company SDC Enterprises Limited, Great Britain. Chemical composition of ECE A standard detergent is shown in Table 1.

**Table 1.** Chemical composition of ECE A non-phosphate reference detergent without optical brighteners

Ingredient	w (%)
Linear sodium alkyl benzene sulphonate (mean length of alkane chain C11.5)	9.7
Ethoxylated fatty alcohol C12-18 (7 EO units)	5.2
Sodium soap, chain length C12-17 46% : C18-20 54%	3.6
Foam inhibitor (DC-4248S)	4.5
Sodium aluminium silicate (Zeolite 4A)	32.5
Sodium carbonate	11.8

Sodium salt of copolymer from acrylic and maleic acid	5.2
Sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 3.3: 1)	3.4
Carboxy methyl cellulose (CMC)	1.3
Diethylene triamine penta (methylene phosphonic acid)	0.8
Sodium sulphate	9.8
Water	12.2
Σ	100.0

Glass fibre filters were purchased from company Munkell, Germany. They have following characteristics: pore size 0.7 µm, thickness 0.24 mm, diameter 47 mm size and particle retention 1.2 µm.

### 2.2. Preparation of PET fibre fragments suspensions

The samples for each standard suspension were cut using microtome. The polyester material was unravelled into isolated fibres. Then fibre threads were compressed firmly into microtome slot. The surplus fibre was cut off from ending side of the microtome plate using a sharp razor blade. A 0.5 mm pusher was for moving forwards the fringe of fibres to project on the opposite side of the holder. Again, the protruding fringe of fibres was cut off using a razor blade. The pieces had a predetermined length equivalent to the length of the pusher (0.5 mm long).

After being cut with a microtome, 4 mg of prepared fibre fragments were dispersed in 800 cm<sup>3</sup> of deionised water (DI). The suspension was shaken in a glass flask with a mechanical stirrer at 250 r.p.m. for 30 min at room temperature. Detergent suspensions were prepared by dissolving 1.00 g of detergent in 800 cm<sup>3</sup> hot tap water so that final concentration of ECE A detergent is 1.25 g dm<sup>-3</sup>. After the detergent has been dissolved, a predetermined amount of particles (m = 4 mg) was added into prepared detergent suspension. The suspension was shaken in a glass flask with a mechanical stirrer at 250 r.p.m. for 30 min at room temperature.

For the assessment of water and detergent suspension stability, the freshly prepared suspension was left to age at room temperature for 5 days.

### 2.3. PET suspensions analysis methods

#### 2.3.1. Particle size analysis (PSA)

The Particle Size Analysis (PSA) was performed according to a standard measurement procedure for each sample in a series of three repetitions on a PSA 1190 LD Anton Paar GmbH, Austria. All measurements were performed in water as solvent, with the stirrer speed and pump speed set to "medium". The measurement is carried out by the laser diffraction method according to The Fraunhofer diffraction theory [14].

The instrument's computer support, the Kalliope® program, displays the measurement results as a distribution function, i.e. particle size distribution (PSD) curve. The characteristic diameters *D*<sub>10</sub>, *D*<sub>50</sub>, *D*<sub>90</sub>, representing 10, 50 and 90% of the particles in that sample smaller than that diameter, as well as average diameter (*A*). The diameters relations are expressed through distribution width (*span value*) and shape factor (*k*) parameters.

#### 2.3.2. Total suspended solids (TSS)

The total suspended solids (TSS) were determined by the standard gravimetric method. Prepared suspensions were subjected to a membrane filtration procedure using glass fibre filter. After filtering the funnel walls were washed with a few millilitres of ethanol (w=96%) in order to recover the possible fibre fragments adhering to the glass. All measurements were done in triplicates.

Finally, filters were dried at 105 °C (± 5°C) until constant mass. Total

suspended solids  $\rho_{TSS}$  ( $\text{mg dm}^{-3}$ ) were calculated by using the following equation:

$$\rho_{TSS} = \frac{(m_2 - m_1)}{V} \cdot 1000$$

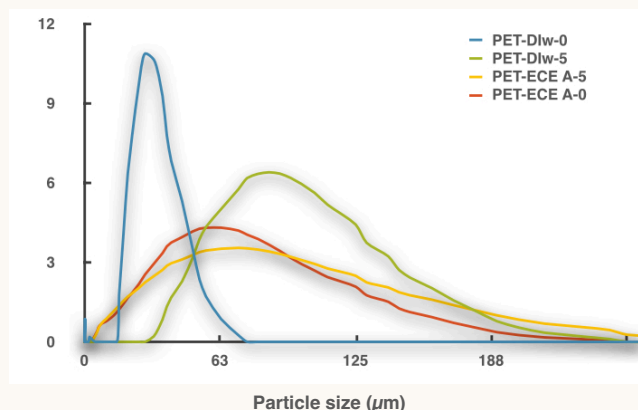
where  $m_2$  and  $m_1$  are the mass of the dry filter after and before the membrane filtration (g), while  $V$  is the volume of filtered suspension ( $\text{dm}^3$ ).

### 2.3.3. Microscope analysis

Dried and cooled down filters were examined with the digital microscope DinoLite digital microscope, Premier IDCP B.V., Almere, The Netherlands under magnification of 50x and 250x. All measurements were done in triplicates.

## 3. Results and discussion

In order to characterise water and detergent suspension, particle size analysis was performed. The results of the particle size analysis in freshly



prepared and 5 days aged water and detergent suspension is shown as PSD curve in Figure 2, and its characteristic parameters, shape factors ( $k$ ) and span values are displayed in Table 2.

**Figure 2.** PSD curve of freshly prepared (signed as 0) and 5 days aged PET (signed as 5) suspension in water and ECE A standard detergent.

**Table 2.** Characteristic parameters of PDS curves for freshly prepared and 5 days aged water and detergent suspensions

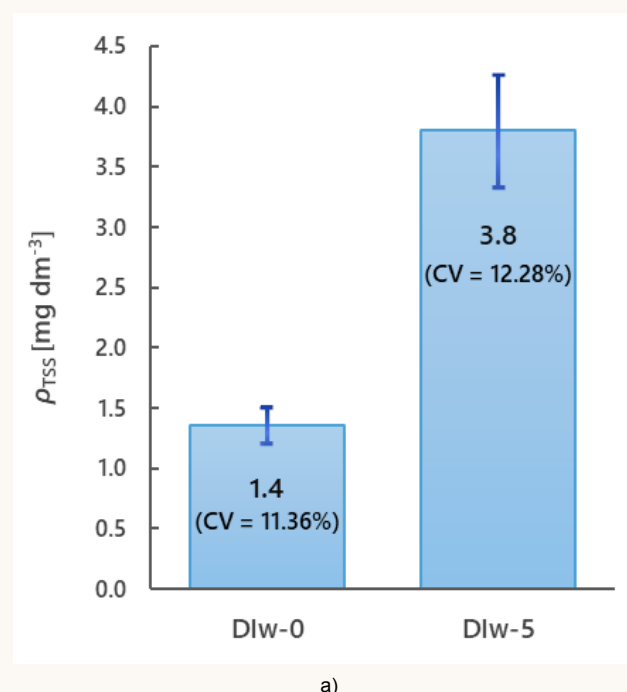
Sample	$D_{10}$ ( $\mu\text{m}$ )	$D_{50}$ ( $\mu\text{m}$ )	$D_{90}$ ( $\mu\text{m}$ )	$A$ ( $\mu\text{m}$ )	$k$	span
PET-Dlw-0	2.69	27.06	42.73	28.49	0.681	1.480
PET-Dlw-5	45.4	79.79	134.9	88.50	1.255	1.120
PET-ECE	13.3	47.30	107.2	57.37	1.510	1.985
PET-ECE	12.6	50.41	130.1	65.15	1.354	2.329

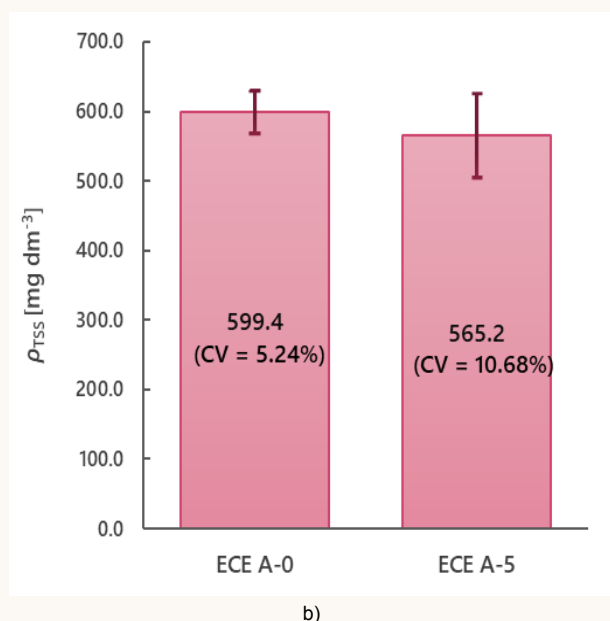
The results are presented as a volume distribution (volume fraction) of particles of a certain size for an interval of specified particle sizes. The PSD curve for freshly prepared PET suspension in water is unimodal with an average particle diameter of 28.49  $\mu\text{m}$ . The PET-Dlw-0 sample is characterised by a narrow range of particle sizes. Most of the FF sizes are in the range of 5-70  $\mu\text{m}$ . Since the PET fibres were cut to a defined length of 500  $\mu\text{m}$ , it can be assumed that the diameters determined correspond to the diameter of the PET fibres. The PSD curves for freshly prepared PET suspensions and aged PET suspensions in water differ in their shape. The curve for the PET-Dlw-5 sample shows a wider range of particle sizes, a smaller volume distribution and a larger mean particle diameter. This can be explained by the fact that this suspension is characterised by larger particles, which may indicate the formation of particle aggregates. Furthermore, PSD curves for freshly prepared and aged PET suspensions with ECE A standard detergent are shown in Figure 2. Since the particle size of the solid detergent components is significantly larger than that of FF-PET (average 28.49  $\mu\text{m}$ ), the PSD

curve represents the volume distribution of the solid detergent particles with an average 57.37  $\mu\text{m}$ . PSD curves for detergent suspension samples take on approximately the same shape, with a slight increase in average particle size (57.37  $\rightarrow$  65.15  $\mu\text{m}$ ) as the suspensions age. Therefore, it is not entirely clear whether the detergent suspension is stable during 5 days of aging or whether the slight increase in the average number of particles is the reason for the formation of aggregates. The influence of particulate matter originating from the detergent on the total particle content in the effluent was observed, so it is necessary to examine in more detail the influence of the detergent and its components on the formation of aggregates of fiber fragments. The content of the prepared PET particles was monitored through the TSS parameter. Suspended matter includes particles larger than 0.45  $\mu\text{m}$ , so the amount of fibrillar PET particles (500  $\mu\text{m}$ ) present in suspensions can correlate to TSS value. Results for freshly prepared and 5 days aged suspension in water and standard ECE A detergent are presented in Table 3 and Figure 3.

**Table 3.** Total suspended solid content for freshly prepared and 5 days aged PET suspensions in water and ECE A standard detergent

Sample	$\rho_{TSS}$ [ $\text{mg dm}^{-3}$ ]	Sample	$\rho_{TSS}$ [ $\text{mg dm}^{-3}$ ]
PET-Dlw-0-a	1.5333	PET-ECE A-0-a	594.0
PET-Dlw-0-b	1.2667	PET-ECE A-0-b	571.0
PET-Dlw-0-c	1.2667	PET-ECE A-0-c	633.1
	$1.3556 \pm 0.1540$ (CV=11.36%)		$599.4 \pm 31.38$ (CV=5.24%)
PET-Dlw-5-a	4.3333	PET-ECE A-5-a	533.1
PET-Dlw-5-b	3.4667	PET-ECE A-5-b	527.6
PET-Dlw-5-c	3.6000	PET-ECE A-5-c	634.8
	$3.8000 \pm 0.4667$ (CV=12.28%)		$565.2 \pm 60.38$ (CV=10.68%)

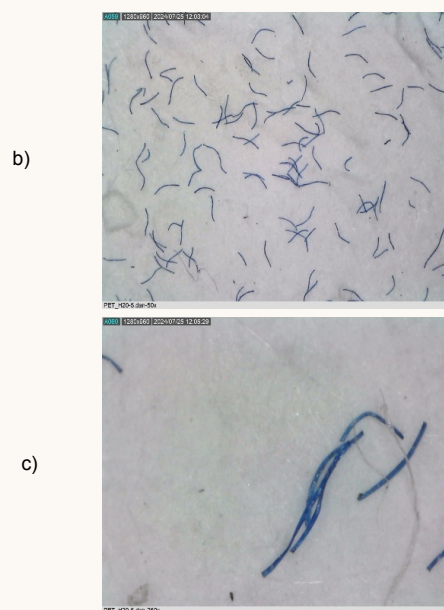




**Figure 3.** Total suspended solid (TSS) content for freshly prepared and 5 days aged PET suspensions in a) water and b) ECE A standard detergent

As mentioned above, suspensions were prepared by adding 4 mg to 800  $\text{cm}^3$  DI water, and it was expected that the TSS value should be about 5  $\text{mg dm}^{-3}$ . However, for the freshly prepared PET- water suspension, the TSS value was 1.36  $\text{mg dm}^{-3}$  with a coefficient of variation of 11.4%. This result is the outcome of several experimental shortcomings. Firstly, dry PET particles have static electricity that interferes with the operation of the balance itself. Therefore, it is not surprising if an error occurs during weighing. To weigh such samples, an ionisation chamber would have to be used to neutralise the static electricity. Another source of error in determining the TSS parameter arises from the nature of the FFs themselves. As already indicated, these are particles whose longitudinal dimension is significantly greater than the transverse dimension. As can be seen from the PSD curves, the diameter of the prepared particles is around 30  $\mu\text{m}$ . So if such a particle encounters a glass fibre filter vertically during the membrane filtration process, it will pass through the pores (45  $\mu\text{m}$ ) unhindered. This leads to an apparently lower content of suspended solids. On the other hand, the TSS values of 3.8  $\text{mg dm}^{-3}$  with a coefficient of variation of 12.3 % were determined by analysing the 5 days aged suspension. If the results of the PSD curve are also taken into account, it becomes clear that when the FF aggregates are formed by standing suspensions, the newly formed aggregates have larger transverse dimensions (approx. 90  $\mu\text{m}$ ), which facilitates their retention on the filters. Total solid content was determined also for PET-ECE A detergent suspensions. The TSS value for the 5- day aged suspension is slightly lower compared to the freshly prepared one, but the data is within the determination error (Figure 3).

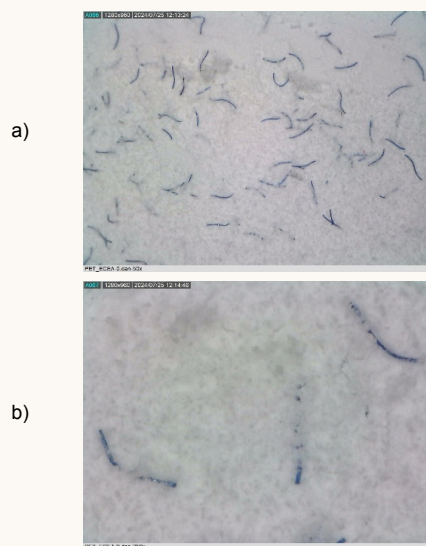
Although the results of the PSD and TSS tests may indicate the formation of aggregates between the particles themselves, but also by detergent components such as surfactants, it is necessary to image filters with isolated particles using a digital microscope to confirm such conclusions. Figure 4 contains digital microphotographs of freshly prepared and 5-day aged PET water suspension.



**Figure 4.** Digital microphotographs of freshly prepared PET water suspension under a) 50x magnification and 5 days aged PET water suspension under b) 50x and c) 250x magnification

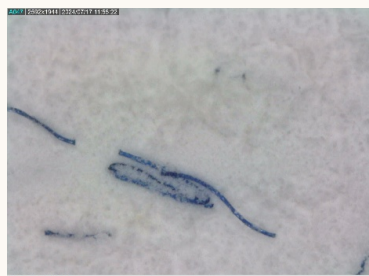
As can be seen, the particles are well distributed on the filter after filtration of the freshly prepared solution, while particle clusters can be observed in the filter for the 5-day aged aqueous suspension (Figure 4c.), which was also observed at 250x magnification. This effect of particle clusters in deionised water can be explained by the fact that PET particles are hydrophobic, so therefore tend to avoid water and form aggregates as a result. Digital microphotographs of the detergent suspension were then taken, which are shown on Figure 4. and Figure 5. It can be seen that insoluble suspended particles from the detergent (e.g. zeolites) partially or completely cover the isolated PET fibre fragments in some places. Thus, the covered particles cannot be accurately identified. Moreover, the detergent component from washing effluents can also significantly interfere and hinder the chemical identification of FF by advanced or proposed methods [1] such as Micro-Fourier Transform Infrared Spectroscopy (micro-FTIR).

Figure 5. shows intertwined PET fibre fragments with solid particles from detergent. Fibrillar microplastic, which include PET fibre fragments, are usually negatively charged. This means that such particles can adhere surfactants [15], which act as a bridge to bind other inorganic substances to FF. This effect is even more pronounced when the suspension is 5 days aged. This fact should also be taken into account when sampling textile washing effluents and characterizing them, as it is obvious that the stability of the suspension changes over time and affects the physicochemical properties of all particles present in the suspension.





c)



**Figure 5.** Digital microphotographs of freshly prepared PET detergent suspension under a) 50x magnification, b) 250x magnification, and c) 5 days aged PET detergent suspension under 250x magnification

## 4. Conclusion

Based on the presented research, it can be concluded that the detergent components present prevent straightforward identification of FF by conventional methods, such as digital microscope and proposed methods for MP identification such as micro-FTIR. In addition, the prepared suspensions show a tendency to form aggregates on ageing, regardless of whether they are aqueous or detergent suspensions, which ultimately makes it difficult to identify and quantify the particles. Therefore, the prepared suspensions are not stable, and it is necessary to prepare them immediately before each analysis.

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